

Study of the morphology of shoe sole composites based on domestic suspension polyvinyl chloride and ethylene-vinyl acetate copolymer

*Sayfullo Musaev**, and *Gulnoz Samiyeva*

Bukhara Engineering-Technological Institute, Bukhara, Uzbekistan

Abstract. The paper studies the surface morphology of the initial polymers and the mixture using a scanning electron microscope SEM - EVO MA 10 (Zeiss, Germany). The X-ray phase analysis was carried out on a Panalytical Empyrean diffractometer. It has been proven that polymer mixtures based on domestic suspension polyvinyl chloride and ethylene-vinyl acetate copolymer, obtained by the method of "thermomechanical" mixing, are two-phase systems consisting of a phase of polyvinyl chloride and an ethylene-vinyl acetate copolymer. It was concluded that suspension polyvinyl chloride is fundamental in this system, which determines the main deformation-strength properties of the mixture. In the process of mixing a certain ratio of copolymer and thermoplastic, two-phase systems are formed, that is, mechanical mixtures of technologically compatible polymers with very close values of solubility parameters are formed. It has been determined that polymer mixtures based on domestic suspension polyvinyl chloride and an ethylene-vinyl acetate copolymer, obtained by the method of "thermomechanical" mixing, are two-phase systems consisting of a phase of polyvinyl chloride and an ethylene-vinyl acetate copolymer.

1 Introduction

An analysis of patent information, domestic and foreign literature made it possible to say that there is a clear lack of information about two-component mixtures of polymers of the PVC-S/SEVA type. To eliminate this problem, it is necessary to consider the mechanisms of formation of mixtures of such polymers, to identify the conditions for the formation of their structure and the temperature ranges of performance. Since a detailed study of the structure will make it possible to explain the mechanism for the appearance of certain deviations of the values of property indicators from the expected ones [1,2].

The study of the structure of two-component polymer compositions using an electron scanning microscope and X-ray diffraction analysis will allow, within its resolution, to observe the overall picture of the structure of the material: the presence of pores, their location, configuration, interconnection, and others [3,4].

* Corresponding author: ssmusaev@rambler.ru

Consideration of films of sample compositions obtained under dynamic conditions and their comparative analysis makes it possible to establish a relationship between the modes of preparation, the amount of modifying additives, and the nature of the microstructure.

It should be noted that the sole materials being developed should meet the requirements of consumers and high-performance technology to the maximum extent while ensuring the high quality of the products.

2 Experimental part

Morphological studies of the initial polymers and composites of the surface of the plates were carried out using a scanning electron microscope SEM - EVO MA 10 (Zeiss, Germany) [5,6].

Taking into account the fact that the samples under study are dielectric (do not conduct electric current), it was necessary to deposit an electrically conductive metal layer to remove the electric charge from the surface of the sample, which is formed under the action of an electron beam formed in the microscope column. The most suitable material for deposition is considered to be metals with a high yield of secondary electrons. The technology of magnetron sputtering was used for sputtering. Metal deposition was carried out on a Quorum magnetron deposition unit, model Q150R ES, using a silver target. Deposition was carried out in an argon gas environment, the thickness was controlled by an electronic sensor. A silver layer 5 nanometers thick was deposited on the surface of the powders under study.

Experiments on a scanning electron microscope were carried out as follows: to carry out the sample preparation process, plates were attached to round holders made of a metal alloy, on top of which a carbon film with a double-sided adhesive surface was glued. During the measurement, an accelerating voltage (EHT – Extra High Tension) of 15.00 kV was applied, the working distance (WD-working distance) was 8.5 mm. The measurement was carried out in the secondary electron detection mode (SED-secondary electrons detector). The images were acquired at various scales using the Smart SEM software.

On Figures 1 show an electron micrograph of cleavages obtained on a scanning microscope from samples of SEVA, PVC-S and mixtures based on them in the ratio PVC-S : SEVA = 0.85 : 0.15.

In all sections of the films, which, when viewed with the naked eye, seem transparent (with varying degrees of transparency), under a microscope, with magnification, one can distinguish geometric shapes of different sizes and configurations. Films obtained on the basis of an ethylene-vinyl acetate copolymer containing 18% vinyl acetate, suspension polyvinyl chloride and a polymer mixture of suspension polyvinyl chloride and an ethylene-vinyl acetate copolymer obtained in a ratio of 85:15 were subjected to microstructural analysis.

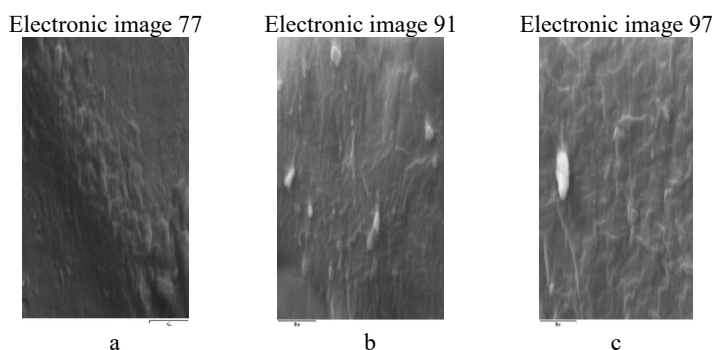


Fig. 1. Micrographs of the surface of SEVA-18 (a), suspension polyvinyl chloride (b) and a two-component polymer mixture of SEVA and PVC-S, obtained at a ratio of 85:15.

Figures 1(a) are micrographs of the surface of an ethylene-vinyl acetate copolymer. The surface of the sample is shiny, which is typical for polyolefins. The surface of the copolymer is not uniform. It can be assumed that the heterogeneity of the structure is associated with the formation of a crystalline supramolecular structure, which is typical for polyethylene (the PE content in the copolymer is 82%).

Figures 1(b) show micrographs of the surface of the suspension polyvinyl chloride. The surface of the sample is matte, oily due to the plasticizer. The white inclusions in the photomicrograph presumably belong to the emulsifiers used in the synthesis of PVC-S.

Figures 1 (c) show a micrograph of the polymer mixture. At a magnification of 2500 times, the structure is monolithic. There are no pores and cracks on the surface, which indicates good compatibility of the components. No heterogeneity was found on the surface of the sample, which indicates the absence of crystalline structures of the polyethylene component of the mixture. X-ray diffraction analysis of the mixture confirms this fact. The surface of the sample is pierced by white threads-strands. The formation of polyolefin fibers/threads is characteristic of blends containing a polyolefin component.

Thus, characterizing the morphology of the structure of polymer mixtures, we can conclude that suspension polyvinyl chloride is fundamental in this system, which determines the main deformation-strength properties of the mixture. In the process of mixing a certain ratio of copolymer and thermoplastic, two-phase systems are formed, that is, mechanical mixtures of technologically compatible polymers with very close values of solubility parameters are formed.

3 Results and discussion

X-ray diffraction can be used to obtain information about the structure and composition of crystalline substances. Most of the joints can be identified using the spacing tables. Diffraction methods (X-ray, neutron diffraction or electron diffraction) have a unique ability to characterize crystalline phases [6-10].

The main advantages of X-ray analysis is that the solid body itself is examined in an unchanged state, and the result of the analysis is the direct determination of the substance or its components. X-rays examine the crystal, i.e. the connection itself. Moreover, in the case of polymorphic bodies, X-rays make it possible to distinguish individual modifications characteristic of a given substance. To study a substance, a very small amount of it is required, which is not destroyed during the analytical operation. Diffraction methods make it possible to detect the slightest changes in the state of the atomic lattice of a crystal that are not detected by other methods. The most widespread is the X-ray powder method, which is mainly used in X-ray phase (X-ray) analysis. This method is currently the most applicable in comparison with other x-ray methods. The explanation for this lies in the fact that many natural and synthetic, technically important materials are most often in a polycrystalline state, and only in this state is it possible to study their structure and properties [11-15].

The Panalytical Empyrean Diffractometer is a compact general purpose X-ray diffractometer with a vertical goniometer and is a system for performing a wide range of analyzes in the field of X-ray diffraction.

The use of a high-precision vertical goniometer allows the analysis of various samples. All control of the equipment operation is carried out by means of a computer on the Data Collector program. It is possible to simultaneously measure and process data using the High Score program with a PDF 2013 database.

Measurements of the phase characteristics of the studied samples were carried out on a Panalytical Empyrean powder X-ray diffractometer. All control over the operation of the equipment is carried out by means of a computer using the Data Collector program, and the analysis of X-ray diffraction patterns was carried out using the High Score program with a

PDF 2013 database. The measurements were carried out at room temperature in the range of 2θ angles in the range from 5° to 90° in the step-by-step scanning mode with a step of 0.013 degrees and a signal accumulation time at each point of 5 s.

X-ray phase analysis of the initial polymers and composites based on them was performed on a Panalytical Empyrean diffractometer, the results of which are shown in Figures 2-5.

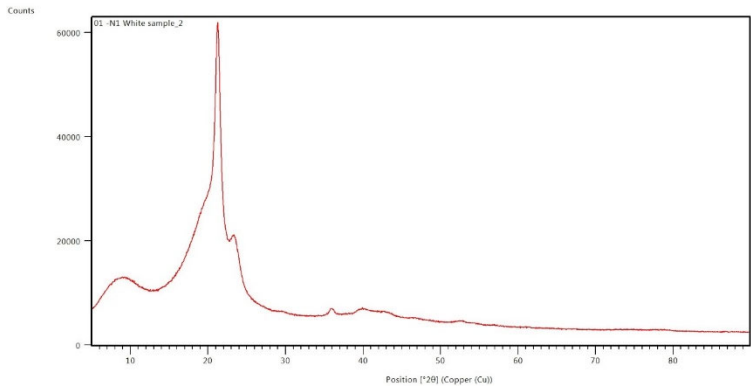


Fig. 2. X-ray pattern of the sample from SEVA-18.

The X-ray diffraction pattern of the initial sample of the ethylene-vinyl acetate copolymer (Figure 2) shows that the presence of a small number of peaks in this X-ray diffraction pattern and the formation of an extended hump in the range of angles of 10–130 indicates an amorphous structure of the presented sample with a small volume of the crystalline phase. The interpretation of diffraction reflections is given in Table 1.

Table 1. Decoding of diffraction reflections SEVA-18.

Sample diffraction reflections				
No.	Pos. [°2θ]	d-spacing [Å]	Height [cts]	FWHM Left [°2θ]
1	9.2186	9.59345	1709.36	0,8817
2	18.9818	4.67544	5352.3	0.8817
3	21.1001	4.2106	14900.6	0.0964
4	21.2246	4.18617	15461.64	0.1515
5	23.2494	3.82599	4318.86	0.6061
6	29.3463	3.04351	348.23	0.8817
7	35.9389	2.49891	617.12	0.3857
8	46.3625	1.95848	273.38	0.8817

On the presented X-ray pattern, 8 peaks were identified, the interference maxima of which are equal to Pos. [°2θ]=9.2186°;18.9818°; 21.1001°; 21.2246°; 23.2494°; 29.3463°; 35.9389°; 46.3625°, with interplanar distances d=9.59345Å, 4.67544Å, 4.2106Å, 4.18617Å, 3.82599Å, 3.04351Å, 2.49891Å, 1.95848Å respectively.

The X-ray pattern of the second component of the polymer mixture of suspension polyvinyl chloride is shown in Figure 3.

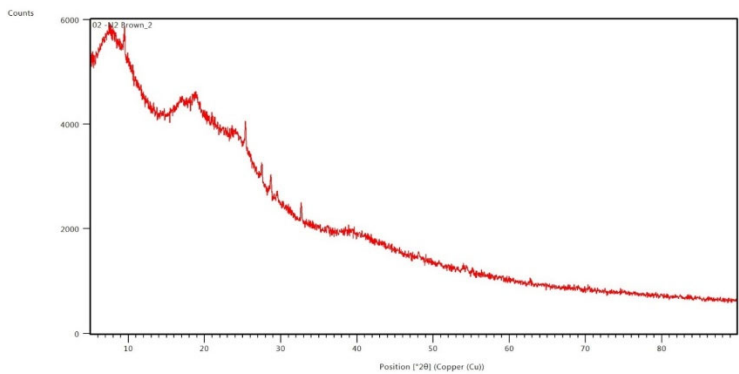


Fig. 3. X-ray diffraction pattern of PVC-S-6346M sample.

The interpretation of diffraction reflections is given in Table 2.

Table 2. Interpretation of diffraction reflections PVC-S-6346M.

Sample diffraction reflections				
No.	Pos. [°2θ]	d-spacing [Å]	Height [cts]	FWHM Left [°2θ]
1	9.4726	9.33676	1026.24	0.1535
2	18.7485	4.73308	892.5	0.614
3	25.3625	3.51182	1105.67	0.1023
4	27.4986	3.24368	512.73	0.1535
5	28.6803	3.11266	387.83	0.1535
6	29.5238	3.02312	128.23	0.09
7	32.6842	2.73992	301.23	0.1279
8	53.9525	1.69811	180.83	0.09

The studied sample is characterized by an amorphous structure. In the amorphous phase, 8 peaks of low intensity are noted: the identified maxima of which are equal to Pos. [°2θ] = 9.4726°, 18.7485°, 25.3625°, 27.4986°, 28.6803°, 29.5238°, 32.6842°, 53.9525° with interplanar distances $d=9.33676\text{Å}$, 4.73308Å , 3.51182Å , 3.24368Å , 3.11266Å , 3.02312Å , 2.73992Å , 1.69811Å respectively.

An X-ray pattern of a polymer mixture based on PVC-S-6346M:SEVA-18 with a component ratio of 85:15 is shown in Figure 4.

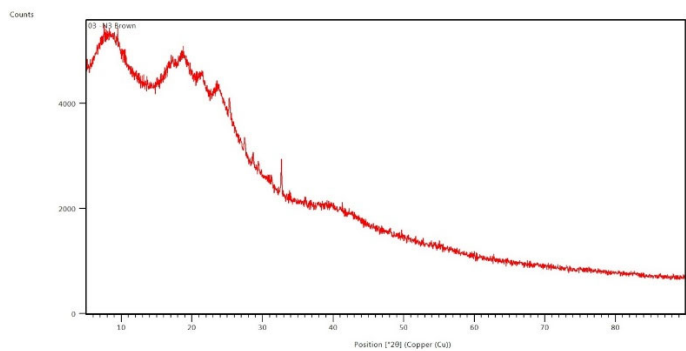


Fig. 4. X-ray pattern of the polymer mixture PVC-S-6346M/SEVA-18.

The interpretation of diffraction reflections is given in Table 3.

Table 3. Interpretation of diffraction reflections of the polymer mixture PVC-S-6346M/SEVA-18.

Sample diffraction reflections				
No.	Pos. [°2θ]	d-spacing [Å]	Height [cts]	FWHM Left [°2θ]
1	18.7103	4.74265	1504	0.921
2	21.2313	4.18488	1323.84	0.614
3	25.3121	3.51869	1218.2	0.1535
4	27.4663	3.24742	603.48	0.2047
5	28.6155	3.11956	381.67	0.307
6	32.6741	2.74074	698.96	0.1023

It can be seen from this figure that the sample is amorphous with 6 low intensity peaks. The identified maxima of which are equal to Pos. [°2θ]= 18.7103°, 21.2313°, 25.3121°, 27.4663°, 28.6155°, 32.6741°, with interplanar distances d=4.74265Å, 4.18488Å, 3.51869Å, 3.24742Å, 3.11956Å, 2.74074Å respectively.

For convenience of analysis, Figure 5 combines two X-ray diffraction patterns for a PVC-S-6346M sample and a polymer mixture based on PVC-S-6346M with SEVA-18.

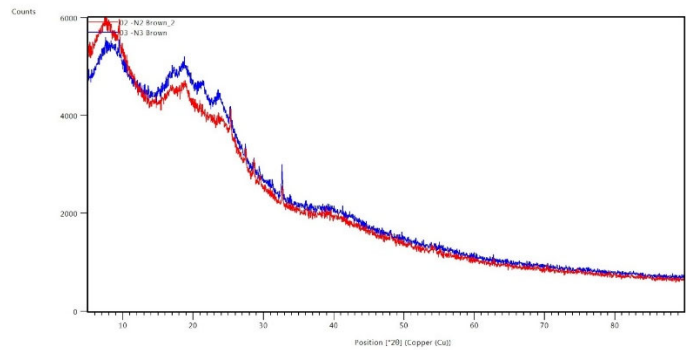


Fig. 5. Combined X-ray patterns of samples of PVC-S-6346M and a polymer mixture based on PVC-S-6346M with SEVA-18.

A comparative analysis of two X-ray patterns Figure 3 and Figure 4 shows that there is an increase in reflexes at angles of 18.7⁰; 21.2⁰, 28.6⁰, 32.6⁰. At the same time, the peaks at 9.4⁰, 29.3⁰ and 53.9⁰ disappeared or decreased to the noise level.

X-ray phase analysis is based on the following principles:

- diffraction pattern is an individual characteristic of a crystalline substance;
- each crystalline phase always gives the same diffraction spectrum, characterized by a set of interplanar distances $d(hkl)$ and corresponding line intensities $I(hkl)$, inherent only to this crystalline phase;
- X-ray diffraction spectrum of a mixture of individual phases is the sum of the diffraction spectra of each phase;
- according to the diffraction spectrum of the mixture, it is possible to quantify the ratio of crystalline phases present in the sample under study.
- The results of X-ray studies are summarized in Tables 4 and 5.

Table 4. Peak analysis of interference maxima Pos. [°2 θ].

SEVA-18	9.21	18.98	21.10	21.22	23.24	-	-	-	29.34	-	35.93	46.36	-
PVC-S-6346M	9.47	18.74	-	-	-	25.36	27.49	28.68	29.52	32.68	-	-	53.95
PVC-S-6346M:SEVA-18= 85:15	-	18.71	-	21.23	-	25.31	27.46	28.61	-	32.67	-	-	-

Table 5. Analysis of interplanar distances $d(\text{\AA})$.

SEVA-18	9.34	4.73	3.51	3.24	3.11	-	-	-	3.11	-	2.74	1.70	-
PVC-S-6346M	9.33	4.73	-	-	-	3.51	3.24	3.11	3.02	2.74	-	-	1.70
PVC-S-6346M:SEVA-18= 85:15	-	4.74	-	4.18	-	3.52	3.25	3.25	-	2.74	-	-	-

Comparing the X-ray patterns of the initial polymers and the polymer composition of the PVC-S-6346M:SEVA-18=85:15 composition, it should be noted:

- for the SEVA-18 component, the crystalline phase disappeared at measurement angles of 9.34° ; 21.10° ; 23.24° ; 29.34° ; 35.93° and 46.36° ; An explanation of the revealed effect of a change in the crystal structure (phase transformation) or distortion of this structure can be the effect of external forces or internal stresses;
- the structure of the PVC-S-6346M matrix has undergone the following changes: peaks in areas 9.47° ; 29.52° and 53.95° have disappeared or decreased to the noise level;
- the appearance of new crystalline formations in the polymer composite was not revealed.

4 Conclusion

Thus, from the point of view of obtaining polymeric materials with uniform technological and operational properties, based on the foregoing, we can conclude that the PVC-S:SEVA=85:15 polymer mixture is suitable as a model system for sole material operated in dry and hot climates. In general, the conducted studies made it possible to determine that polymer mixtures based on domestic suspension polyvinyl chloride and an ethylene-vinyl acetate copolymer, obtained by the method of "thermomechanical" mixing, are two-phase systems consisting of a phase of polyvinyl chloride and an ethylene-vinyl acetate copolymer. The system is a crystalline polymer with a degree of crystallinity of 18%.

References

1. K. B. Kalmykov, N. E. Dmitrieva, *Scanning electron microscopy and X-ray -spectral analysis of inorganic materials* (Moscow State University named after M.V. Lomonosov, Moscow, 2017)
2. S. S. Musaev, G. O. Samiev, L. S. Musaeva, *The study of the structure of the polymer composition based on suspension PVC and the Copolymer EVA*. International Scientific and Technical Conference "Design, Technology and Innovation in Textile and Light Industry" (Innovation - 2022). Moscow, 213-215 (2022)
3. E. R. Galimov, K. V. Kormushin, Z. Ya. Khalitov, *X-ray diffraction analysis of polycrystals*. Textbook (Kazan, publishing house of KSTU, 2006)
4. V. Sh. Shekhtman, R. A. Dilanyan, *Introduction to X-ray crystallography* (ISSP RAS, Chernogolovka - Ed. Department of IPChV RAS, 2002)
5. S. S. Musaev, G. O. Samieva, *REVISTA, Leather and Footwear Journal*. Bucharest, Romania, Europe **21(4)**, 247-256 (2021)
6. D. Yu. Pushcharovsky, *X-ray of minerals* (M. CJSC "Geoinformmark", 2000)
7. G. H. Michler, *Electron Microscopy of Polymers* (Springer, 2010).
8. L. C. Saywer, D. T. Grubb, G. F. Meyers, *Polymer microscopy* (Springer, New York, 2008)
9. A. Zankel, M. Nachtnebel, C. Mayrhofer, K. Wewerka, *Deformation and Fracture Behaviour of Polymer Materials*, **2020** 95-108 (2020)

10. J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. E. Lyman, E. Lifshin, L. Sawyer, J. R. Michael, *Scanning Electron Microscopy and X-Ray Microanalysis* (Academic/Plenum Publishers, New York, 2003)
11. G. B. Bokiy, M. A. Poray-Koshits, *X-ray diffraction analysis* (Publishing House of Moscow State University, Moscow, 1984)
12. R. F. Grossman, Per. from English, ed. Guzeeva V.V. *Guidelines for the development of compositions based on PVC*. (Scientific foundations and technologies, St. Petersburg, 2009)
13. N. A. Kozlov, A. D. Mitrofanov, *Physics of polymers* (Proc. allowance / Vladim. state un-t; Vladimir, 2001)
14. T. J. Kadirov, M. Chorlieva, F. U. Nigmatova, M. A. Mansurova, Modern Innovations, Systems and Technologies **2(4)**, 0401-0411 (2022). <https://doi.org/10.47813/2782-2818-2022-2-4-0401-0411>
15. S. Mardonov, K. Saidov, Modern Innovations, Systems and Technologies **1(3)**, 65-69 (2021). <https://doi.org/10.47813/2782-2818-2021-1-3-65-69>